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(54) Title of the Invention: Photo-setting Composition for Dental Material

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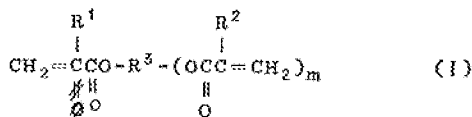
Specification

1. Title of the Invention:

Photo-setting Composition for Dental Material

2. We claim:

A photo-setting composition for a dental material, comprising: (A) 50 weight % or more of a liquid thioether type polymerizable monomer produced by the addition reaction of (1) a polyene compound (I) represented by the following general formula (I):

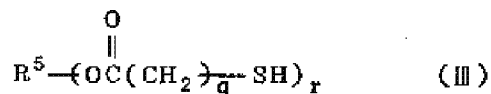


(wherein: R¹ and R² may be the same or different and are H or CH₃; R³ is a C₂₋₂₀ substituted or unsubstituted aliphatic polyvalent alcohol residue or substituted or unsubstituted polyalkylene ether polyol residue, wherein OH may be contained; and m is an integer of 1 or 2) with (2) a polythiol compound (II) represented by the following general formula

(II):



(wherein: R⁴ is a C₂₋₁₀ substituted or unsubstituted polyvalent aliphatic hydrocarbon residue, wherein OH may be contained; and p is an integer of 1 to 4) and/or (3) a polythiol compound represented by the following formula (III):



(wherein: R⁵ is a C₂₋₂₀ substituted or unsubstituted aliphatic polyvalent alcohol residue, wherein OH may be contained; q is an integer of 1 or 2; and r is an integer of 1 to 4) in the presence of a basic catalyst, wherein the functional group equivalent ratio of the polyene compound (I) to the polythiol compound (II) and/or polythiol compound (III) is 2 to 10; and (B) 50 weight % or less of a polymerizable polyfunctional vinyl monomer.

3. Detailed Explanation of the Invention

[Industrial Field of Application]

The present invention relates to a photo-setting composition for a dental material, particularly to a photo-setting composition for a dental material suitable for composite resin for teeth, tooth crown resin, resin for denture base and the like, having improved polymerization curability at normal temperature or thereabout and giving a cured product having improved curability and hardness.

[Prior Art]

A large number of proposals have conventionally been made that use photo-setting compositions for composite resin for teeth, tooth crown resin, resin for denture base and the like. However, all of these are made of a polymerizable monomer such as methacrylic acid ester and a photoinitiator. For example, in Published Unexamined Patent Application Nos. S52-101894, S57-82305 and S61-44910, methacrylic acid ester of glycidyl ether of bisphenol A is used as a polymerizable monomer. However, this polymerizable monomer tends to change color into yellow by light,

(3)

Moreover, methods of using aliphatic polyfunctional methacrylic acid esters as polymerizable monomers are disclosed in Published Unexamined Patent Application Nos. S56-26809, S57-77608 and the like. However, these aliphatic polyfunctional methacrylic acid esters are expensive and generally have high melting points or are highly viscous and, therefore require a reactive diluent. In other words, the problem is that those esters cannot be used alone. The use of a reactive diluent is not preferable because the rigidity and toughness of a cured product decline.

Moreover, Published Unexamined Patent Application Nos. S60-231605, S57-38791, S57-154114 and the like disclose methods of using polyfunctional methacrylic acid ester having a phosphate backbone. However, strength and hardness are not sufficient in this polymerizable monomer alone though it is well adhesive to tooth substances, and therefore a polymerizable monomer such as methacrylic acid ester of glycidyl ether of bisphenol A is additionally required. However, the use of methacrylic acid ester of glycidyl ether of bisphenol A has the disadvantage that it tends to change color into yellow by ultraviolet light.

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particularly by ultraviolet light. In addition, this polymerizable monomer is highly viscous and, therefore, has a problem with containing air bubbles during operation. Hence, aliphatic methacrylic acid ester of low density is used as a reactive diluent. However, the use of such a reactive diluent is not preferable because high rigidity and toughness, which a cured product of methacrylic acid ester of glycidyl ether of bisphenol A otherwise has, declines.

Methods for enhancing strength and hardness by making a urethane bond by reacting an aromatic or aliphatic monofunctional or polyfunctional isocyanate with a polyfunctional methacrylic acid ester having alcoholic hydroxide are disclosed in Published Unexamined Patent Application Nos. S55-83706, S61-15807, S61-179215 and the like. However, a urethane bond is susceptible to hydrolysis in the presence of an acid and, therefore, is not suitable as a dental material. Additionally, an aromatic isocyanate is not preferable because it tends to change color into yellow.

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It goes without saying that methacrylic acid esters of aliphatic polyfunctional alcohols significantly contracts at the time of curing and are inferior in terms of adhesion to tooth substances, dimension stability, breakage at the time of curing, and the like.

Excellent mechanical properties of a cured product such as hardness and strength are required in addition to curability and adhesion to tooth substances at normal temperature or thereabout. However, those requirements have not sufficiently been satisfied.

Although it was attempted to improve the abovementioned disadvantages by combining two types or more of methacrylic acid ester monomers, such an attempt was not necessarily successful.

As described above, conventional photo-setting composition for dental materials are not good enough to be used as composite resin for teeth, tooth crown resin and resin for denture base in terms of mechanical properties such as hardness and strength. There is a need for the development of improved dental materials.

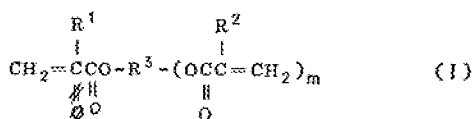
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Furthermore, there are some technologies proposed in which a polyene compound and a polythiol compound are radically polymerized with a radical initiator or chemically active energy beams such as ultraviolet light to make macromolecular sulfide compounds to be used as printing materials, paints, adhesives, molding materials and the like (Published Unexamined Patent Application Nos. S53-28959 and S53-134096).

These methods disclose technologies for producing solid polythioether having a reticular molecular structure, wherein no unreacted ene or thiol group is substantially contained because of cross-linking binding reaction between polyene and polythiol. In order to achieve this purpose, the molar ratio of a reactive carbon-carbon unsaturated group to a thiol group must be 0.75/1 to 1.5/1. It is described that the molar ratio should be selected for each composition such that cross-linked solid products can be produced after the completion of curing reaction. However, there is no description of the method according to the present invention. That is, the disclosures describe neither a method for producing a liquid thioether type polymerizable monomer having a vinyl group on its terminal by addition reaction in the presence of a basic catalyst, wherein the ratio of total number of vinyl groups of a polyene compound represented by the

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In other words, the present invention relates to a photo-setting composition for a dental material, comprising: (A) 50 weight % or more of a liquid thioether type polymerizable monomer produced by the addition reaction of (1) a polyene compound (I) represented by the following general formula (I):



(wherein: R¹ and R² may be the same or different and are H or CH₃; R³ is a C₂₋₂₀ substituted or unsubstituted aliphatic polyvalent alcohol residue or substituted or unsubstituted polyalkylene ether polyol residue, wherein OH may be contained; and m is an integer of 1 or 2) with (2) a polythiol compound (II) represented by the following general formula (II):



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general formula (I) to the total number of thiol groups of polythiol compounds represented by the general formulae (II) and (III) (referred to hereinafter as "functional group equivalent ratio") is in the range of 2 to 10, nor a method for producing a liquid thioether type polymerizable monomer by the addition reaction of specific polyene and polythiol compounds.

(Problems that the Invention is to Solve)

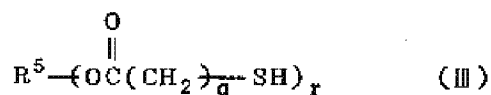
The purpose of the present invention is to provide a photo-setting composition for a dental material, having improved polymerization curability at normal temperature or thereabout as well as improved curability and hardness.

[Means of Solving the Problems]

The present inventors intensively studied ways of solving the disadvantages associated with conventional photo-setting compositions for dental materials. As a result, they found that a composition consisting of (A) a liquid thioether type polymerizable monomer produced by the addition reaction of a polyene compound and a polythiol compound in the presence of a basic catalyst, wherein a molecular terminal is capped with a polymerizable vinyl group, and (B) a polymerizable polyfunctional vinyl monomer can effectively achieve the abovementioned purpose. Thus, the present invention was completed.

(8)

(wherein: R⁴ is a C₂₋₁₀ substituted or unsubstituted polyvalent aliphatic hydrocarbon residue, wherein OH may be contained; and p is an integer of 1 to 4) and/or (3) a polythiol compound represented by the following formula (III):



(wherein: R⁵ is a C₂₋₂₀ substituted or unsubstituted aliphatic polyvalent alcohol residue, wherein OH may be contained; q is an integer of 1 or 2; and r is an integer of 1 to 4) in the presence of a basic catalyst, wherein the functional group equivalent ratio of the polyene compound (I) to the polythiol compound (II) and/or polythiol compound (III) is 2 to 10; and (B) 50 weight % or less of a polymerizable polyfunctional vinyl monomer.

As polyene compounds (I) used in the present invention, which is represented by the abovementioned general formula (I), it is preferred to select monomers having P.I.I values of not more than 2 in order to minimize irritation to oral mucous membranes. Additionally, it is preferred to select monomers that have a high boiling point and are odorless or less odorous.

As used herein, P.I.I refers to the skin primary irritation index. The skin irritability is mild when P.I.I is not more than 2, medium when P.I.I is 3 to 6, and severe when P.I.I is 7 to 8.

Such polyene compounds (I) include diethylene glycol methacrylate, 1, 3 – butanediol methacrylate, triethylene glycol methacrylate, tetraethylene glycol methacrylate, 2 – hydroxypropyl – 1, 3 – dimethacrylate, 1, 6 – hexane dimethacrylate, neopentyl glycol dimethacrylate, pentaerythritol tri(meth)acrylate, trimethylolpropane triacrylate, dipentaerythritol hexa(meth)acrylate, and tripropylene glycol diacrylate.

Polyole compounds represented by the abovementioned general formula (II) include propane – 1, 2 – dithiol, n – hexane – 1, 6 – dithiol, ethanedithiol, neopentane – 1, 3 – dithiol, propane – 1, 3 – dithiol, and cyclohexane – 1, 4 –

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The addition reaction of a polyene compound and a polythiol compound is conducted in the presence of a basic catalyst. Basic catalysts include conventionally well-known basic ion exchange resin, potassium, tert – butoxide, phosphine type compounds and amine type compounds. Particularly preferable are phosphine type compounds or amine type compounds.

Phosphine type compounds include triphenylphosphine, tri – n – butylphosphine and triethylphosphine. Amine type compounds include pyridine, N, N – dimethylaniline, N, N – diethylaniline, trimethylamine, triethylamine, tri(n – propyl)amine, tri(iso – propyl)amine, tri(n – butyl)amine, tri(iso – butyl)amine, tri(sec – butyl)amine, dimethylethylamine, diethylmethylamine, triethanolamine, dimethylethanolamine, monomethyldiethanolamine, and diethylamine.

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dithiol.

Polythiol compounds represented by the abovementioned general formula (III) include ethylene glycol dithioglycolate, diethylene glycol dithioglycolate, trimethylolpropane trithioglycolate, trimethylolpropane dithioglycolate, neopentyl glycol tetrathioglycolate, pentaerythritol tetrathioglycolate, and trimethylolpropane trithiopropionate.

At the time of producing a liquid thioether type polymerizable monomer by the addition reaction of a polyene compound (I) and a polythiol compound (II) and/or a polythiol compound (III), the functional group equivalent ratio of the polyene compound (I) to the polythiol compound (II) and/or the polythiol compound (III) is in the range of 2 to 10. If the functional group equivalent ratio is smaller than 2, gelation may occur depending on the type of compounds and combination thereof. On the other hand, if the functional group equivalent ratio exceeds 10, the viscosity of a liquid thioether type polymerizable monomer thus produced is too low though the addition reaction of a polyene compound and a polythiol compound occurs easily. Thus, the disadvantage is that operability declines (e.g., liquid dripping).

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These basic catalysts can be used singly or by combinations thereof. The used amount cannot necessarily be specified because it varies depending on the types, combinations and used amounts of a polyene compound (I) and a polythiol compound (II) and/or a polythiol compound (III) to be used. Nevertheless, it is 0.01 to 3 weight %, preferably 0.03 to 1 weight % relative to the total amount of a polythiol compound (II) and/or a polythiol compound (III). If the amount of a basic catalyst is less than 0.01 weight %, it does not essentially serve as a catalyst, and vinyl groups of a polyene compound (I) are often polymerized. On the other hand, if it exceeds 3 weight %, it does not show the effect of a large amount. Moreover, it is not preferable because coloration occurs. Additionally, it is not preferable because a large amount of a remover is required after reaction.

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In the case of removing a basic catalyst after reaction, well-known methods for adsorption, extraction and vacuum aspiration may be used within the limits that do not influence polymerization on the following step. Particularly, in the case of removing an amine type compound, it can be adsorbed and removed using neutral alumina, acidic alumina, or acidic ion exchange resin. If an amine type compound has a low boiling point, it may be removed by the vacuum aspiration method.

The temperature of addition reaction cannot necessarily be specified because it varies depending on combinations and compounding ratios of a polyene compound (I) and a polythiol compound (II) or the type and amount of a basic catalyst. Nevertheless, it is normally 0 to 100°C, preferably 20 to 60°C. The temperature of addition reaction exceeding 100°C is not preferable because gelation often occurs, though the polymerization of vinyl groups of a polyene compound may be prevented depending on the type and amount of a basic catalyst. On the other hand, the temperature of addition reaction at 0°C or below is not preferable because the reaction speed is low, though the addition reaction proceeds.

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The polymerizable polyfunctional vinyl monomer may be the same compound as the abovementioned polyene compound (I). Also included are bis (β - acryloyloxyethyl) phthalate, 2, 2 - bis [4 - (β - (meth) acryloyloxydiethoxy) phenyl] propane, 2, 2 - bis [4 - (6 - (meth) acryloyloxy - β - hydroxypropoxy) phenyl] propane, and ditrimethylolpropane tetrahydrophthalate tetra(meth)acrylate.

The mixing ratio of a liquid thioether type polymerizable monomer and a polymerizable polyfunctional vinyl monomer is at least 50 weight % of the liquid thioether type polymerizable monomer to at most 50 weight % of the polymerizable polyfunctional vinyl monomer. The mixing ratio of a polymerizable polyfunctional vinyl monomer that is more than 50 weight % is not preferable because the contraction percentage of a cured product becomes so large that adhesion with tooth substances declines.

Although the photo-setting composition for a dental

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It is preferred that addition reaction be conducted in an inert atmosphere in order to prevent the production of disulfide arising out of autooxidation of a polythiol compound (II) and/or a polythiol compound (III).

A liquid thioether type polymerizable monomer thus produced has a structure in which the molecular terminal is capped with a polymerizable vinyl group and is excellent at storage stability. This liquid thioether type polymerizable monomer may contain an unreacted polyene compound depending on the feed molar ratio of a polyene compound and a polythiol compound. This unreacted polyene compound may be removed as needed or may be used without being removed as a mixture with the liquid thioether type polymerizable monomer. In the present invention, both of these cases are referred to as liquid thioether type polymerizable monomers.

The photo-setting composition for a dental material according to the present invention may be the abovementioned liquid thioether type polymerizable monomer alone or may be mixed with a polymerizable polyfunctional vinyl monomer.

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material according to the present invention has photo-setting properties itself, a generally used photoinitiator may optionally be added to give sufficient curability. Moreover, the photo-setting composition for a dental material may be added with fillers, pigments, x-ray contrast media as needed.

The types and amounts of these fillers are not particularly limited as far as they do not adversely influence curability and coloration (and outer appearance) of a cured product before and after the irradiation of light. Photoinitiators include α -diketones such as camphorquinone, benzyl and benzyl dimethyl ketal, benzoin such as benzoin and benzoin isopropylether, disulfides such as diphenyl disulfide and tetramethylthiuram disulfide, and benzophenones such as thioxanthone and 4, 4' - dimethylamino benzophenone. Tertiary amines such as triethanolamine and dimethylethanolamine may be used together in order to enhance the efficiency of these photoinitiators.

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Thermal initiators include peroxides such as benzoyl peroxide, lauroyl peroxide and di-tert-butyl peroxide, and azo compounds such as 2, 2 – azobisisobutyronitrile, 2, 2 – azobiscyclohexanecarbonitrile. Moreover, room temperature setting type polymerization initiators such as benzoyl peroxide and aromatic tertiary amines may be used together.

Fillers include organic fillers such as polymethyl methacrylate, and inorganic fillers such as glass powder, glass flake, anhydrous silica, silica hydrate, starch silica, alumina, calcium phosphate, quartz sand, quartz and talc. Pigments may be selected from yellow, brown, gray and pink, which match the color tone of tooth substances.

X-ray contract media include a wide variety of insoluble barium salts.

The light source used for curing the photo-setting composition for a dental material according to the present invention varies depending on the application of the composition. Generally included are visible light lamps, low-pressure, high-pressure or ultrahigh-pressure mercury

lamps, xenon lamps, metal halide lamps and arc lamps. The optimal amount of irradiation and irradiation speed of activation energy light beams may optionally be decided in view of the coloration and outer appearance of a cured product.

[Examples]

Next, a description of the present invention is given below in more detail with reference to examples. We evaluated cured products and liquid thioether type polymerizable monomers by the following test methods.

(1) Compression strength, tensile strength, bending strength and flexure

We complied with the method described in JIS K 6911.

(2) Knoop hardness

We complied with the method described in JIS Z 2251.

(3) Hardness depth

We filled a mold having a diameter of 4mm with paste, irradiated visible light downward for 40 seconds and then measured the length (mm) of a cured portion from the surface.

(4) Consistency (mm)

We evaluated the spread of 0.5g of paste in terms of diameter (mm) by applying 1kg of a load for 5 minutes.

(5) Coloration

We observed coloration (X) or without coloration (○) visually before and after the irradiation of ultraviolet light.

(6) Analysis of thiol group

A: titration method (Valhard method)

We dissolved 1 to 2g of a liquid thioether type polymerizable monomer sample by adding 10mL of toluene and 10mL of ethanol. We then added 10mL of 0.1 N AgNO₃, followed by an iron alum indicator. Next, we performed back titration for excess AgNO₃ using 0.025N NH₄SCN to analyze the residual amount of the thiol group. We then calculated the relative rate of decrease (rate of reaction) of the thiol group based on the amount at the time of feeding.

B: Raman spectroscopy

We analyzed a gelated sample by the Raman spectroscopy (R-800 model manufactured by JASCO Corporation). We then calculated the degree of reaction of the

thiol group based on the relative rate of decrease from the monomer state with regard to the ratio of the absorption of the thiol group at 1570cm⁻¹ to the absorption of the carbonyl group at 1730 cm⁻¹.

(7) Analysis of vinyl group

We followed ¹H-NMR (R-24B model manufactured by Hitachi Ltd.) for a sample that was not gelated or followed the Raman spectroscopy for a gelated sample and calculated the degree of reaction of the vinyl group based on the relative rate of decrease from the monomer state with regard to the ratio of the absorption of the vinyl group at 1620cm⁻¹ to the absorption of the carbonyl group at 1730 cm⁻¹.

(8) Storage stability

We preserved a liquid thioether type polymerizable monomer by allowing it to stand in the air at 40°C and measured time required for the occurrence of gelation. We used a symbol (⊙) if it is 20 hours or more, a symbol (○) if it is 10 to 20 hours, a symbol (△) if it is 1 to 10 hours and a symbol (X) if it is 1 hour or less.

Production Example 1

After feeding 700g of diethylene glycol methacrylate to a 2L separable flask equipped with a stirrer and an addition funnel at room temperature, we dissolved it by adding 1g of diethylamine while stirring. Next, we added 300g of ethylene glycol dithioglycolate dropwise over 30 minutes. We stirred at room temperature until exothermal reaction stopped. After the end of the exothermal reaction, we stirred at 40°C for 10 hours. After the end of reaction, we added 50g of an inorganic adsorbent for adsorbing strong bases (Kyowado 700SL manufactured by Kyowa Chemical Industry Co., Ltd.) to remove diethylamine. We then filtered off the adsorbent to obtain a liquid polymerizable monomer mixture.

¹H-NMR:

1.2 to 1.35 (m, α-methyl proton when β-methylene of methacryloyl is added to thiol); 1.9 to 2.03 (d, α-methyl proton of methacryloyl); 2.5 to 3.1 (m, methylene proton next to α-methyl and β-methylene proton when β-methylene of

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methacryloyl is added to thiol); 3.23 to 3.33 (methylene proton next to thiol of ethylene glycol dithioglycolate); 3.5 to 4.5 (proton of ethoxy of diethylene glycol dimethacrylate and ethylene glycol dithioglycolate); 5.5 to 6.2 (β-methylene proton of methacryloyl).

Raman spectra:

The absorption of thiol at 1570 cm⁻¹ disappeared.

The degree of reaction of the vinyl group originated from methacryloyl was 66.6% based on an integral curve of ¹H-NMR, which agreed well with the theoretical degree of reaction 66.0% when it was supposed that 100% of the thiol group reacted. Furthermore, we measured the thiol group in the liquid polymerizable monomer by the titration method (Volhard method) to find that the degree of reaction of the thiol group was 99.0%. In other words, the residual thiol group was substantially zero.

Accordingly, it is obvious that a polymerizable monomer mixture having a polythioether backbone was produced.

(24)

Production Examples 2-8

We conducted addition reaction in a manner similar to Production Example 1 except for the conditions of polyene compounds, polythiol compounds, basic catalysts, addition reaction temperatures, and addition reaction periods, which are shown in Table 1. Table 1 shows the results.

All of these results substantially suggest that polymerizable monomer mixtures having a polyether backbone have been obtained.

Reference Examples 1-3

We conducted addition reaction in a manner similar to Production Example 1 except for the conditions as shown in Table 1.

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Table 1

	Polyene compounds (parts by weight)	Polyol compounds (parts by weight)	Functional group equivalent ratio (---)	Catalyst (parts by weight)	Temperature (°C)	Time (hr)	Thiol group reaction ratio (%)	Storage stability
Production Example 1	DEGDMA 700	EGDTGA 300	2.0	Diethylamine 1	40	3	99.0	○
Production Example 2	NPGDMA 800	TMPTTGA 200	4.3	Diethylamine 1	40	4	99.2	○
Production Example 3	2HPDMA 900	PETTGA 100	8.5	Diethylamine 2	40	3	99.3	○
Production Example 4	TMPTMA 900	EGDTGA 100	8.4	Diethylmethylamine 1	30	2.5	99.5	○
Production Example 5	DEGDMA 700	DPHTGA 300	2.2	Diethylmethylamine 2	30	3.5	99.0	○
Production Example 6	TMPTMA 800	EGDTGA 200	3.7	Diethylmethylamine 2	40	2	99.4	○
Production Example 7	NPGDMA 700	PETTGA 300	2.1	Diethylmethylamine 1	40	3	99.1	○
Reference Example 1	HDMA 550	TMPTTGA 450	1.1	Diethylamine 1	40	4	Gelation 99.2	---
Reference Example 2	TMDTMA 500	DPHTGA 500	1.0	Diethylamine 2	20	3	Gelation 65.0	---
Reference Example 3	DEGDMA 750	TMPTTGA 250	2.8	---	50	8	48.5	X

DEGDMA: diethylene glycol dimetacrylate
NPGDMA: neopentyl glycol dimetacrylate
HDMA: 1, 6 – hexane dimetacrylate
TMPTMA: trimethylolpropane trimetacrylate
DPHA: dipentaerythritol hexaacrylate
2HPDMA: 2 – hydroxyl propane dimetacrylate

EGDTGA: ethylene glycol dithioglycolate
 TMPTTGA: trimethylolpropane trithioglycolate
 PETTGA: pentaerythritol tetrathioglycolate
 DPHTGA: dipentaerythritol hexathioglycolate

Example 1

We added 40 parts by weight of 2, 2 – bis [4 – (τ – methacryloyloxy – β - hydroxypropoxy) phenyl] propane to 60 parts by weight of the polymerizable monomer mixture having a polythioether backbone obtained in Production Example 1. After dissolving, we added 400 parts by weight of starch silica having a particle size of 0.2 to 2μ to adjust its consistency. We further added 0.4 parts by weight of camphor quinone as a catalyst, 0.2 parts by weight of triethanolamine and 0.2 parts by weight of benzoin isopropyl ether to make a paste.

We filled a mold made of Teflon having an inner diameter of 4mm and a depth of 3mm with this paste. After placing a transparent film made of polypropylene on the upper face, we irradiated visible light for about 1 minute using a visible light irradiator (Translux ® manufactured by Kulzer Inc.) to make a test specimen.

Table 2 shows the results.

Examples 2-7

We performed polymerization in a manner similar to Example 1 except that each polymerizable monomer mixture having a polythioether backbone obtained in Production Examples 2-7 was used in place of the polymerizable

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monomer mixture having a polythioether backbone obtained in Production Example 1. Table 2 shows the results.

Comparative Examples 1-3

We compounded 2, 2 – bis [4 – (τ – methacryloyloxy – β - hydroxypropoxy) phenyl] propane, 2, 2 – bis [4 – (ω – methacryloyloxy polyethoxy) phenyl] propane and trimethylolpropane trimetacrylate at the ratios as shown in Table 2. After dissolving, we treated them under the conditions similar to Example 1 to obtain test specimens. Table 2 shows the results.

As shown in Table 2, hardness is particularly low in Comparative Example 1; a cured product is fragile in Comparative Example 2; and coloration is marked and consistency low in Comparative Example 3. Accordingly, they cannot be used as photo-setting compositions for dental materials.

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Comparative Example 4

We performed polymerization in a manner similar to Example 1 except that we used 60 parts by weight of 2, 2 – bis [4 – (τ – methacryloyloxy – β - hydroxypropoxy) phenyl] propane relative to 40 parts by weight of the polymerizable monomer mixture having a polythioether backbone obtained in Production Example 1. Table 2 shows the results.

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Table 2

	Production No. of polymerizable monomer mixture	Consistency of paste (mm)	Physical properties of cured products					Reference
			Hardness depth (mm)	Compression strength (kg/cm ²)	Tensile strength (kg/cm ²)	Knoop hardness (---)	Coloration	
Example 1	1	15.0	7.3	3400	520	57.0	○	
Example 2	2	26.2	7.2	3600	607	58.7	○	
Example 3	3	32.1	7.5	3700	630	59.2	○	
Example 4	4	26.9	7.0	3500	550	63.3	○	
Example 5	5	16.2	8.0	3600	600	57.9	○	
Example 6	6	23.8	7.0	3500	540	59.4	○	
Example 7	7	20.0	8.2	3750	650	60.2	○	
Comparative Example 1	BPE2HPPMA 50 BPEPEGMA 30 TMPTMA 20	26.8	7.0	3200	500	48.4	○	
Comparative Example 2	BPE2HPPMA 10 BPEPEGMA 10 TMPTMA 80	42.2	90 (Cured products were broken.)	3300	460	62.0	○	Cured products are very fragile.
Comparative Example 3	BPE2HPPMA 40 BPEPEGMA 50 TMPTMA 10	10.2	6.2	3100	510	47.8	X	
Comparative Example 4	1	42	8.0	3000	500	45.0	X	

BPE2HPPMA: 2, 2 - bis [4 - (τ - methacryloyloxy - β - hydroxypropoxy) phenyl] propaneBPEPEGMA: 2, 2 - bis [4 - (ω - methacryloyloxy polyethoxy) phenyl] propane

TMPTMA: trimethylolpropane trimetacrylate

Example 8

We added 20 parts by weight of polymethyl methacrylate (molecular weight: 10,000) and 70 parts by weight of Aerosil (Aerosil RM-50 manufactured by Japan Aerosil Co., Ltd.) to 100 parts by weight of the polymerizable monomer mixture produced in Production Example 3 to make consistency substantially uniform. Next, we added 0.1 parts by weight of benzophenone as a catalyst and 0.05 parts by weight of tri-n-octylphosphite as a coloration stabilizer to obtain a paste.

We filled a mold made of Teflon with this paste. After placing a transparent film made of polypropylene on the upper face, we irradiated ultraviolet light for about 2 hours using a 20W chemical lamp to make a test specimen.

Examples 9-11

We performed polymerization under the conditions similar to Example 8 except that we used polymerizable monomer mixtures obtained in Production Examples 4, 5 and 6. Table 3 shows physical property values of cured products thus obtained.

Comparative Examples 5-6

We performed polymerization under the conditions similar to Example 8 except for the conditions as shown in Table 3.

Table 3 shows physical property values of cured products thus obtained.

Comparative Example 5 was low in hardness. Comparative Example 6 had coloration. Accordingly, they are not suitable for composite resin used for a tooth crown.

(31)

(32)

Table 3

	Production No. of polymerizable monomer mixture	Consistency of paste (mm)	Physical properties of cured product			
			Bending strength (kg/cm ²)	Flexure (mm)	Knoop hardness (—)	Coloration
Example 8	Production Example 3	16.3	580	1.00	26.1	○
Example 9	Production Example 4	15.5	620	1.03	23.4	○
Example 10	Production Example 5	12.2	660	0.99	27.3	○
Example 11	Production Example 6	15.2	620	1.02	28.4	○
Comparative Example 5	Reference Example 1	16.0	570	1.01	20.0	○
Comparative Example 6	Reference Example 3	15.2	520	1.02	21.2	X

(33)

As described above, it is obvious that the photo-setting compositions for dental materials according to the present invention are suitable for composite resin for teeth and tooth crown composite resin based on Examples 1-7 and suitable for resin for denture base based on Examples 8-11.

[Effect of the Invention]

The photo-setting compositions for dental materials according to the present invention are excellent at polymerization curability at normal temperature or thereabout as well as hardness and strength and, therefore, can solve the problems of the abovementioned conventional photo-setting compositions for dental materials.

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